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PARTIAL PRESSURE OF SO_2 IN SODIUM BISULFITE-SULFITE SALTS SOLUTION

REPORT No. 91-166-K

Shinn-Der Chang
Process Chemistry Section
Chemical Research Department

ABSTRACT

The partial pressure of SO2 in sodium bisulfite-sulfite salt solution was reviewed and investigated by US EPA extensively and reported by D.K. Oestreich in 1976 (EPA-600/2-76-279). In the experiments the data reported covers pH range 4-6 and ionic strength up to 10 and in the correlation a chemical equilibrium consisting of SO_2 and bisulfite in an ideal solution was considered. It was found in the present investigation that this correlation can predict the partial pressure fairly well for conditions of pH below 6. It cannot predict the partial pressure accurately for conditions of pH above 6 where most high alkalinity scrubbers are normally operating. A new correlation was thus developed based on a non-ideal solution consisting of SO_2 and active species, sodium bisulfite, and sulfite and inactive species, sodium sulfate, and chloride in chemical equilibrium. The new correlation can be applied to the entire range of conditions of these species in chemical equilibrium.

job	file	date	report no.
31-570-400	837.24122	December 6, 1991	91-166-K

92-04123/

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EXECUTIVE SUMMARY

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Shinn-Der Chang
Process Chemistry Section

In a gas side resistance limited mass transfer system the concentration difference between the gas phase and the equilibrium interface is the driving force for the mass transfer from gas to liquid. A high alkalinity flue gas desulfurization process such as dual alkali FGD is exactly in this category. The difficulty of SO_2 absorption may be measured in terms of the Number of Transfer Units (NTU), the natural logarithm of the ratio of the driving force at the inlet to the driving force at the outlet. If the SO_2 partial pressure in the flue gas above the scrubbing liquor is equal to the equilibrium partial pressure of SO_2 there will be no driving force and no SO_2 removal. Therefore, the equilibrium partial pressure of SO_2 must be known accurately in order to design an efficient and economic SO_2 absorber.

The partial pressure of SO_2 over sulfite-bisulfite solutions was reviewed and investigated by the US EPA extensively and reported by Oestreich in 1976(1). In that investigation, experimental data reported covers the pH range from 4-6 and the ionic strength up to 10 and in the correlation, the chemical equilibrium of SO_2 and bisulfite was considered. It was found that this correlation can predict the equilibrium SO_2 partial pressure fairly well for conditions of pH below 6. It is not surprising that it cannot predict the partial pressure accurately for conditions of pH greater than 6 where sulfite ions are present in significant quantity and were not considered in the original correlation. Because most high alkalinity scrubbers normally operate at pH greater than 6, a new correlation is needed. A method based on a real solution consisting of SO_2, and active species, sodium sulfite and sodium bisulfite and inactive species, sodium sulfate, and sodium chloride in chemical equilibrium, closely simulating the FMC dual alkali system, was developed in this work and is presented in this report.

The major findings are summarized as follows.

The vapor pressure model developed in this work appears to represent well the data of Johnstone et al. and also can predict well the TWR-EPA field tests data. The model, however, under predicts the EPA reported data and the FMC published data. The relatively higher data points may be attributed to the uncertainty of the sampling technique employed in the original investigations.

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The EPA-FMC model was derived based on a simplified ideal solution model and excluding $SO_3^=$ in the formulation, therefore it can not be extrapolated to pH values greater than 6.

The model developed in this work based on a non-ideal solution model can predict vapor pressure well over the entire range of pH where most dual alkali processes are operating. This model is recommended to be used for the process design.

In the scrubbing of SO_2 from stack gas the difference of the partial pressure of SO_2 in the gas and the partial pressure of SO_2 in equilibrium with the SO_2 dissolved in the liquid is the driving force for SO_2 absorption. This partial pressure must be known accurately in order to design a viable absorber. Using the more accurate vapor pressure correlation from this work would result in savings in the design NTU required. A saving in the design NTU required would result in savings in the capital investment and the operating cost of the absorber.

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To

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PARTIAL PRESSURE OF SO_2 IN SODIUM BISULFITE-SULFITE SALTS SOLUTION

Shinn-Der Chang

1.0 INTRODUCTION

In a gas side resistance limited mass transfer system the concentration difference between the gas phase and the equilibrium interface is the driving force for the mass transfer from gas to liquid. A high alkalinity flue gas desulfurization process such as dual alkali FGD is exactly in this category. The difficulty of SO_2 absorption may be measured in terms of the Number of Transfer Units (NTU), the natural logarithm of the ratio of the driving force at the inlet to the driving force at the outlet. If the SO_2 partial pressure in the flue gas above the scrubbing liquor is equal to the equilibrium partial pressure of SO_2 there will be no driving force and no SO_2 removal. Therefore, the equilibrium partial pressure of SO_2 must be known accurately in order to design an efficient and economic SO_2 absorber.

The partial pressure of SO_2 over sulfite-bisulfite solutions was reviewed and investigated by the US EPA extensively and reported by Oestreich in 1976(1). In that investigation, experimental data reported covers the pH range from 4-6 and the ionic strength up to 10 and in the correlation, the chemical equilibrium of SO_2 and bisulfite was considered. It was found that this correlation can predict the equilibrium SO_2 partial pressure fairly well for conditions of pH below 6. It is not surprising that it cannot predict the partial pressure accurately for conditions of pH greater than 6 where sulfite ions are present in significant quantity and were not considered in the original correlation. Because most high alkalinity scrubbers normally operate at pH greater than 6, a new correlation is needed. A method based on a real solution consisting of SO_2, and active species, sodium sulfite and sodium bisulfite and inactive species, sodium sulfate, and sodium chloride in chemical equilibrium, closely simulating the FMC dual alkali system, was developed in this work and is presented in this report.

2.0 VAPOR PRESSURE OF SO_2 OVER SODIUM SULFITE AND BISULFITE LIQUOR

The solubility of SO_2 in the sodium sulfite-bisulfite liquor is very dilute and Henry's law can normally be applied. The concentration of H_2SO_3 is governed by the chemical equilibrium between SO_2, and the species dissolved in the liquor. Thus, if the concentration of H_2SO_3 and its activity coefficient

can be determined the equilibrium partial pressure of SO_2 in the scrubbing liquor can be calculated from the following equation,

$$(1) \quad p_{SO_2} = K_o \, \alpha_{H_2SO_3} = K_o \, \gamma_{H_2SO_3} [H_2SO_3]$$

Where K_o is the Henry's law constant and α and γ are the activity and activity coefficient respectively.

The total solubility of SO_2 in the molecular form and as H_2SO_3 may be calculated from the chemical equilibrium as is shown in the following section.

3.0 CHEMICAL EQUILIBRIUM IN THE DUAL ALKALI SCRUBBING LIQUOR

$$SO_2 + H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons H^+ + SO_3^=$$

Considering the chemical equilibrium above, the following relationships hold.

$$(2) \quad [HSO_3^-] = K_1 \, \alpha_{H_2SO_3} / \alpha_{H^+} / \gamma_{HSO_3^-}$$

$$(3) \quad [SO_3^=] = K_1 K_2 \, \alpha_{H_2SO_3} / (\alpha_{H^+})^2 / \gamma_{SO_3^=}$$

The electron neutrality will also hold for the liquor, or,

$$(4) \quad [Na^+] + [H^+] = [HSO_3^-] + 2[SO_3^=] + 2[SO_4^=] + [Cl^-]$$

Among the above four equations there are six unknown quantities in addition to two inactive components. They are defined as follows:

$[H^+] = m_1$
$[Na^+] = m_3$
$[HSO_3^-] = m_4$
$[SO_3^=] = m_2$
$[H_2SO_3] = m$
P_{so2}

and

$$[SO_4^{=}] = m_6$$
$$[Cl^-] = m_8$$

Where m_x is the molarity of species x in the solution.

In addition:

$$(5) \quad \alpha_x = \gamma_x[x] = \gamma_x m_x$$

$$(6) \quad \alpha_{H^+} = 10^{-pH}$$

Alternatively, instead of electron neutrality a material balance of the total oxidizable sulfur can be considered,

$$(7) \quad [TOS] = [H_2SO_3] + [HSO_3^-] + [SO_3^=]$$

Then, with these definitions the above equations can be rewritten and solved for m in the following forms:

$$(8) \quad m\,\gamma_{H_2SO_3} = \frac{[m_3 + m_1 - 2m_6 - m_8]}{\frac{K_1}{10^{-pH}\,\gamma_{HSO_3^-}} + \frac{2K_1K_2}{(10^{-pH})^2\,\gamma_{SO_3^=}}}$$

or

$$(9) \quad m\,\gamma_{H_2SO_3} = \frac{TOS}{\left[\frac{1}{\gamma_{H_2SO_3}} + \frac{K_1}{10^{-pH}\,\gamma_{HSO_3^-}} + \frac{K_1K_2}{(10^{-pH})^2\,\gamma_{SO_3^=}}\right]}$$

Since m_1 is small and negligible compared to m_3 in a concentrated dual alkali system, the m_1 may be dropped from the numerator term in Equation (8). The numerator (M_3 - $2M_6$ - M_8), can be recognized simply as the active sodium concentration.

Assuming that the activity coefficients can be calculated at given liquor compositions, only three unknowns in each equation, [Na^+, act], pH, and m in equation (8) and [TOS], pH, and m in equation (9), remain to be determined. If two of the three quantities are assigned , the system is therefore fully defined and all unknowns can then be calculated. The other equations required are

given in appendix A. With the newly calculated liquor composition a new set of activity coefficients can be obtained. The calculations can be repeated until the changes of the composition from the last calculation are within a specified tolerance. Then, Equation (1) can be applied to obtain the vapor prssure required.

4.0 ACTIVITY COEFFICIENTS

The method to evaluate the activity coefficients of a strong electrolyte in aqueous solutions with a very high ionic strength was investigated and reported by Meissner et al. (2,3,4) and by Bromley (5). The Bromley method is in an analytical form and is convenient to use. In this method the activity coefficient of each strong electrolyte in aqueous solution is correlated into a Debye-Huckel type equation with a single characteristic parameter B for each electrolyte applicable to an ionic strength up to about six. The system of multi-component salt solutions was recommended to be treated as a single complex salt with a characteristic temperature dependent constant B to be included in the following equations:

$$(10) \quad \log \gamma_{HSO_3^-} = -\frac{AI^{1/2}}{1+I^{1/2}} + \left[\frac{0.06 + 0.6B}{(1+1.5I)^2} + B\right] ([H^+] + [Na^+])$$

$$(11) \quad \log \gamma_{SO_3^=} = -\frac{4AI^{1/2}}{1+I^{1/2}} + \left[\frac{0.12 + 1.2B}{(1 + 0.75I)^2} + B\right] (2.25)([H^+]+[Na^+])$$

where A is the Debye-Huckel constant and is defined in Equation (12)

$$(12) \quad A = 263.1/T^{2/3}$$

$$(13) \quad B = 4(2.25\, B_{32}\, m_3\, m_2 + 2.25\, B_{36}\, m_3\, m_6 + B_{34}\, m_3\, m_4 + B_{38}\, m_3\, m_8)/(m_3 + m_2 + m_4 + m_6 + m_8)/(m_3 + 4m_2 + m_4 + 4m_6 + m_8)$$

and I is the ionic strength in the solution and B_{ij} is the characteristic constant of the ionic pair i and j.

For an undissociated species, H_2SO_3, the activity coefficient can be approximated to be unity.

5.0 LITERATURE REFERENCES

Experimental determination of the partial pressure of SO_2 over sulfite-bisulfite solutions is extremely difficult since the values under conditions of interest are always lower than 1 mm Hg and therefore difficult to measure and analyze directly.

Two establis' ed laboratory methods were frequently employed: one was the dynamic method and the other was the static method. In addition, there was also a field method to calculate the vapor pressures from a plant trial. Three typical examples are briefly described as follows:

5.1 Johnstone et al. (6)

Along with their development of processes for the recovery of sulfur dioxide from waste gases, Johnstone et al. also measured and reported vapor pressure data of sulfur dioxide in sodium sulfite-bisulfite solutions. A dynamic method was employed.

The dynamic method uses a transpiration technique by bubbling an inert gas such as nitrogen through the scrubbing solution. The SO_2 gas carried along with the carrier gas is trapped and analyzed iodometrically. The advantage of this method is its ability to accumulate sufficient quantity of SO_2 suitable for a wet analysis. However, if too much SO_2 is extracted from the solution, the total oxidizable sulfur level in the solution may be altered and if the carrier gas passes through the solution too quickly the system may not reach equilibrium and/or may carry some entrained mist. A slight carryover of solution would seriously affect the quality of the experiment.

In the Johnstone et al. work, commercial grade chemicals were used without further purification and 0.1% hydroquinone was added to prevent oxidation. The results were correlated based on a simplified ideal solution model in contrast to the highly non-ideal scrubbing solution under consideration.

This work was reviewed by Oestreich of EPA (1) and it was found that vapor pressure of SO_2 in the liquor was insensitive to the changes of sulfur (IV) concentration as shown in Figure 1. Nevertheless, the experiment covered four temperature levels and offered invaluable information on the temperature effect on the system. More comments on this work will follow in Section 6.

5.2 EPA Study (1)

In their review of Johnstone's work the EPA concluded that the inaccuracy was due to the dynamic method employed in the experiments. EPA repeated the measurements but the dynamic method was replaced by a static method.

The static method adopted by EPA used Teder bags as the equilibrium vessels. Experiments began with the bag to be loaded with simulated liquor in such a fashion as to avoid the introduction of oxygen or carbon dioxide into the vessel. Then the bag was placed in a constant temperature bath and given two hours to reach equilibrium. Finally a vapor sample was taken and analyzed chromatographically for the SO_2 content.

The advantage of this method is that equilibrium is assured and a desired liquid composition can be maintained. The disadvantages are that sampling by syringe is required and a slight drop of syringe temperature may condense the moisture and result in a higher reported SO_2 partial pressure. The accuracy of the data is limited by the accuracy of the analysis which was estimated by EPA to have a coefficient of variation of 6.9%.

5.3 TRW-EPA Field Tests at FMC Pilot Plant

In 1977 TRW conducted a test program for the EPA to evaluate and classify all boiler emissions on

coal and oil fired boilers with and without FGD equipment. Continuous samplers were used to obtain data for inlet and outlet concentrations of SO_2, NO_x, CO and hydrocarbons. The tests were carried out at the FMC pilot plant at the Firestone Tire and Rubber Plant, Pottstown, Pennsylvania on October 6, 1977 (7).

The tests began with soda ash fed to the recirculation tank. The bleed flow and the regeneration return flow were shut off to allow the solution pH to drop. Continuous outlet SO_2 concentrations were reported. Once the pH dropped to 5.6 and the outlet SO_2 concentrations had risen sharply, the bleed flow, the soda ash feed and the regeneration flow were restored. As the pH was allowed to rise, the outlet SO_2 concentrations were monitored. The results are shown in Figure 2 and listed in Appendix B. It is very interesting to note that the values obtained from increasing pH coincided with the values obtained from decreasing the pH. It suggests that a true equilibrium existed during the tests.

The inlet SO_2 concentration was 1098 vppm, moisture 13%, and the temperature was 50 to 53 °C. The scrubber was a venturi type running at 24" WG pressure drop. By assuming NTU available and employing the number of transfer units concept the equilibrium SO_2 vapor pressure at the outlet conditions can be calculated. The results are also listed in Appendix C.

6.0 RESULTS

The SO_2 vapor pressure model described in Section 2 was tested and compared with reported literature data in this section. The numerical constants employed in the calculation are summarized in Table 1.

The data of Johnstone et al. (6) is shown in Figure 3, a plot of SO_2 vapor pressure versus total oxidizable sulfur concentrations using temperature and active sodium concentration as the parameters. The vapor pressure increases with increases of oxidizable sulfur and temperature while holding the other parameters constant. The trends of the effects of each parameter are quite apparent and appears to be a better way to represent date than that shown in Figure 1, which does not illustrate the effect of oxidizable sulfur concentration.

Equation (1) was applied to Johnstone et al. data to calculate K_o for each data point. The results were correlated by means of least squares into equation (14),

$$(14) \qquad K_o = \exp(a - b/T)$$

and $a = 12.5$
$b = 1868$
K_o is in mm Hg/mol

Using these best-fit values the vapor pressures were calculated at conditions which coincided with Johnstone et al. observations. The solid lines shown in Figure 3 represent these calculated results. The same set of data was plotted again in Figure 4 to compare the calculated values with the observed values. They agree very well with each other.

EPA data were shown in Figures 5 and 6 for two levels of oxidizable sulfur as a function of pH values. Vapor pressure seems to decrease with increases in pH but it appears to deviate from the EPA-FMC linear relationship with pH (1). The calculated values from equation (1) using a=12.5 are also included in the same figure and are always lower than the observed values. The calculated values could be forced to fit the observations by adjusting the K_o value but no obvious argument can be found to support such an adjustment. On the contrary, the sampling procedure employed in the original investigation is suspected to cause moisture to condense and may result in higher reported values as discussed in the earlier section.

FMC published four data points in the early '70's (8) and these are reproduced in Figure 7. The calculated values are shown by the solid lines. With a=12.5 obtained from the best fit of the Johnstone et al. data the calculated values seem to be lower than the observed values. It would fit well if the "a" value was adjusted to 12.7. It is suspected that moisture condensation in sampling similar to that in the EPA trials may have resulted in high readings.

The vapor pressure data calculated from TWR-EPA field tests at the FMC pilot plant located at Firestone Tire and Rubber Plant at Pottstown, Pennsylvania were also compared with the calculated values from equation (1) which are shown in Figure 8 as a solid line. The calculated values from EPA-FMC correlation also are shown in the same figure in dashed lines. The solid line obtained from the present work agrees well with the data points. The solid line and data points fall within the calculated EPA bounds at pH's below 6 and are lower and outside the EPA bounds for pH's greater than 6.

As discussed earlier, the difficulty of the SO_2 removal can be expressed in terms of the NTU required. Taking into account the effect of pH on the vapor pressure of SO_2, the pH effect on the NTU required can be calculated. Using % S in coal as the parameters and with 95% SO2 removal specified this effect is shown in Figure 9. The solid lines in the figure represent NTU based on the vapor pressure of SO_2 calculated from this work and the dashed lines represent NTU based on the EPA data. We may see that at a specified sulfur level in coal the NTU required decreases with increases of pH. At constant pH the NTU increases with decreasing sulfur levels in the coal.

If it is assumed that for 2.5% S coal applications the inlet and outlet SO_2 concentrations are 1724 vppm and 86.2 vppm respectively and at pH 6.2 the NTU required is 3.79, calculated based on 48.5 vppm vapor pressure from this work and 5.19 calculated based on 77 vppm vapor pressure from the EPA-FMC model. Using the newly developed model would result in a saving in NTU of 27%.

For 1% S coal application the inlet SO_2 concentration is 700 vppm and pH is 6.5 the NTU required would be 3.54 using data from this work and 7.30 using data from the EPA-FMC model. The difference would be 3.76 NTU, a saving in NTU of 52%.

7.0 CONCLUSIONS AND SIGNIFICANCES

The vapor pressure model developed in this work appears to represent well the data of Johnstone et al. and also can predict well the TWR-EPA field tests data. The model, however, under predicts the EPA reported data and the FMC published data. The relatively higher data points may be attributed to the uncertainty of the sampling technique employed in the original investigations.

The EPA-FMC model was derived based on a simplified ideal solution model and excluding $SO_3^=$

in the formulation, therefore it can not be extrapolated to pH values greater than 6.

The model developed in this work based on a non-ideal solution model can predict vapor pressure well over the entire range of pH where most dual alkali processes are operating. This model is recommended to be used for the process design.

In the scrubbing of SO_2 from stack gas the difference of the partial pressure of SO_2 in the gas and the partial pressure of SO_2 in equilibrium with the SO_2 dissolved in the liquid is the driving force for SO_2 absorption. This partial pressure must be known accurately in order to design a viable absorber. Using the more accurate vapor pressure correlation from this work would result in savings in the design NTU required. A saving in the design NTU required would result in savings in the capital investment and the operating cost of the absorber.

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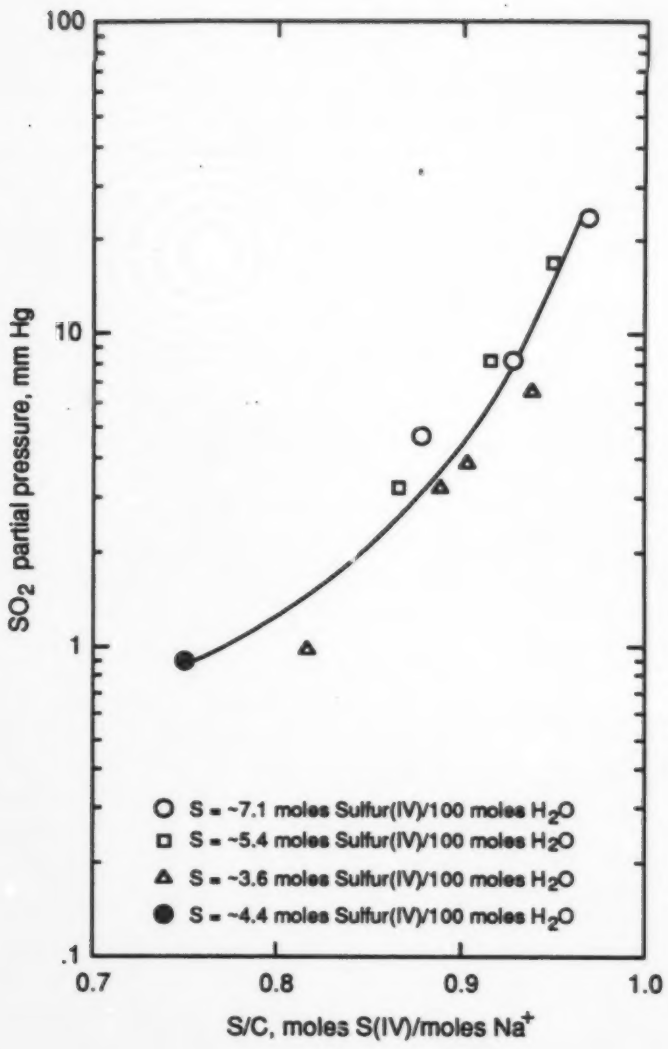

FIGURE 1

JOHNSTONE'S DATA FOR Na_2SO_3 /$NaHSO_3$ SYSTEM AT 90°C

TABLE 1

NUMERICAL PARAMETERS EMPLOYED IN THIS WORK

Parameters	References
$l_n K_o = 12.48 - 1868/T$	(6)
$l_n K_1 = -10967 + 1972.5/T$	(9)
$pK_2 = -\log_{10} K_2 = 5.47 + 288/T$	This work
$A = 0.511$ at 25°C	(11)
$A = 263.1/T^{1.5}$	(10,11)
$B_{32} = -0.0282$	(11)
$B_{34} = -0.0374$	(11)
$B_{36} = -0.0204$	(5)
$B_{38} = 0.0574$	(5)

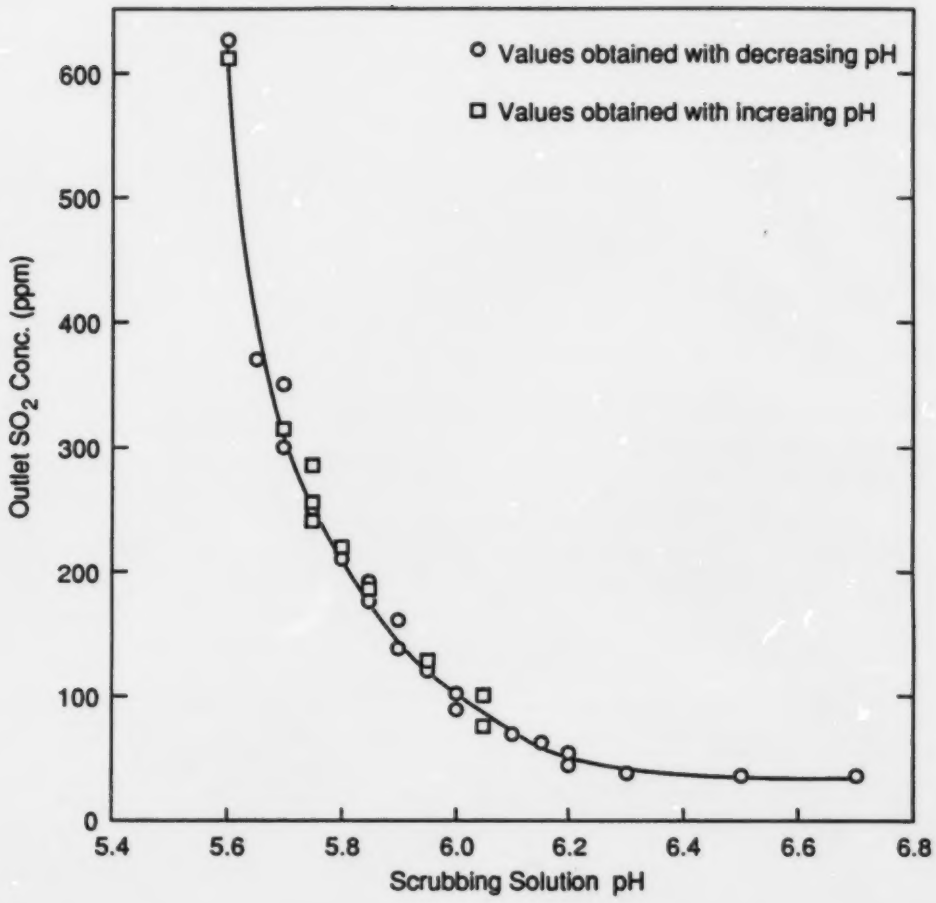

FIGURE 2

OUTLET SO_2 CONC. VS. SCRUBBING SOLUTION pH

Average Inlet SO_2 - 1098 ppm
Outlet gas flow - 7000 Acfm
Liquor flow - 116 gpm
Solution chemistry

Na_2SO_3	0.414 M
$NaHSO_3$	0.398 M
Na_2SO_4	0.415 M

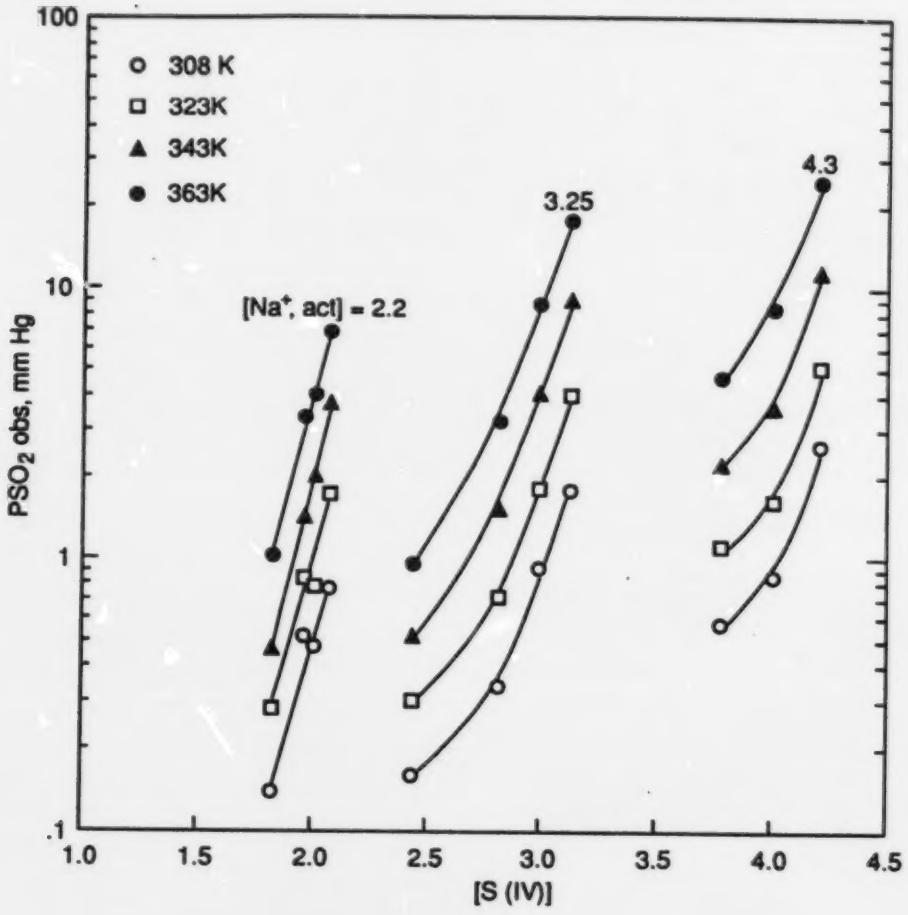

FIGURE 3

CALCULATE VAPOR PRESSURE OF SO_2 FROM [S (IV)] & [Na+, act] IN SOLID LINES COMPARED TO DATA POINTS OF JOHNSTONE et al. (6)

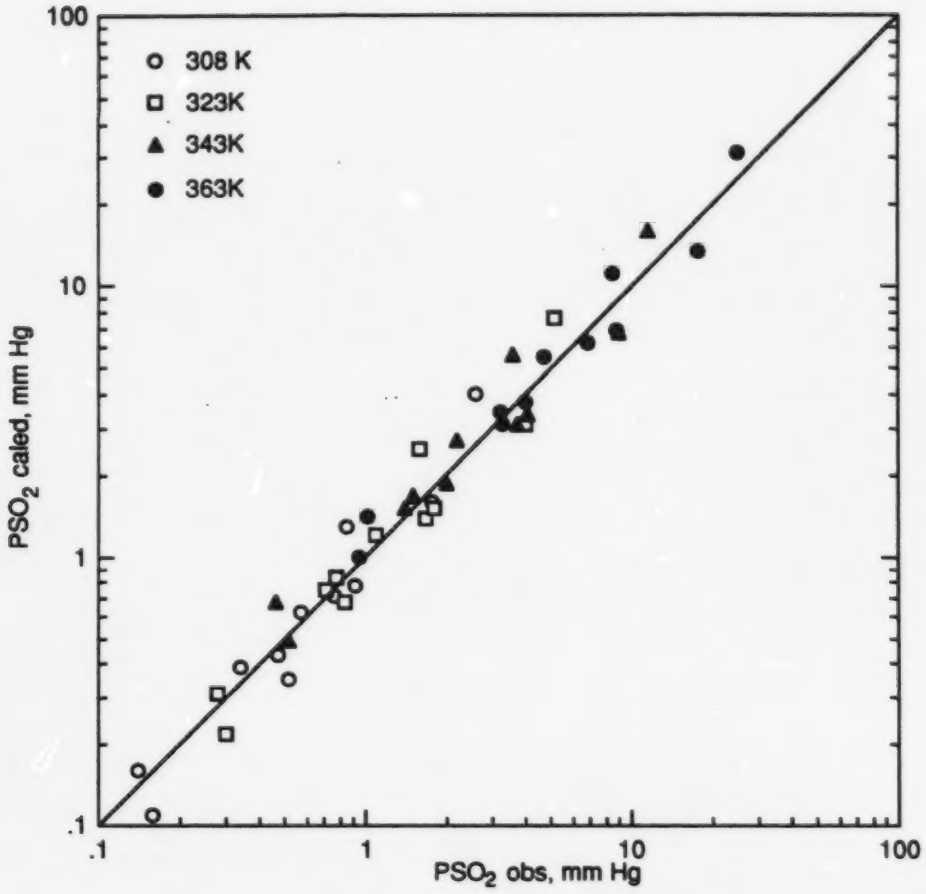

FIGURE 4

CALCULATED VAPOUR PRESSURE OF SO_2 COMPARED TO REPORTED BY JOHNSTONE ET AL .(6)

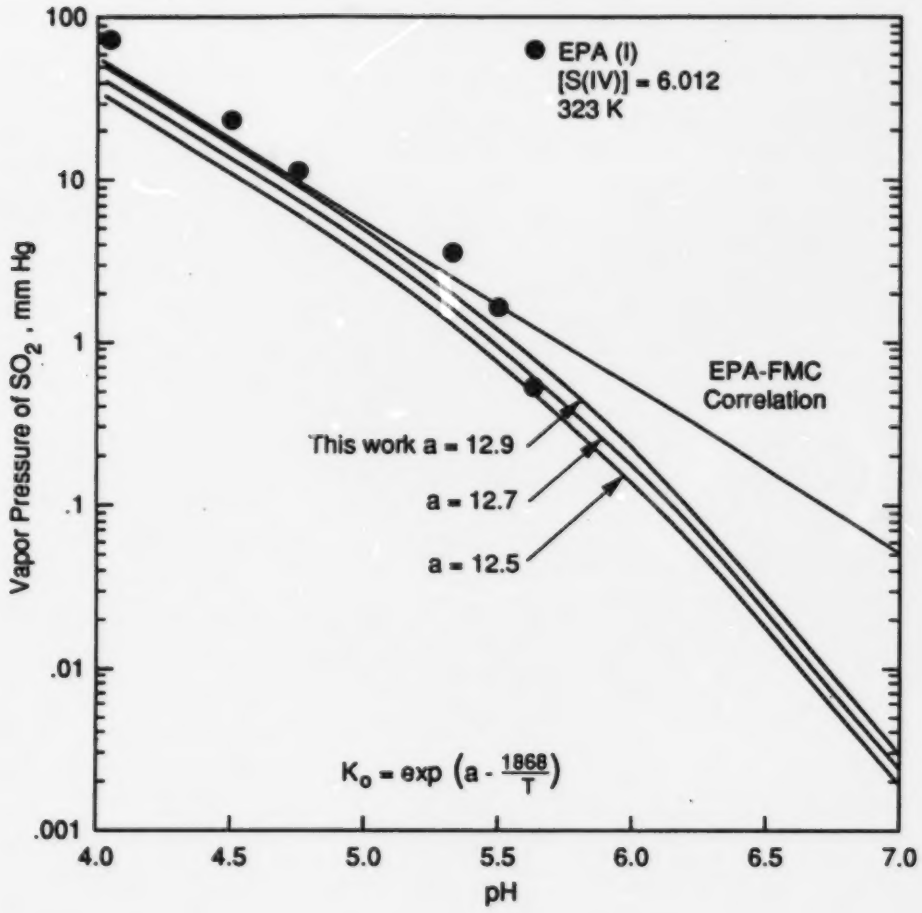

FIGURE 5

VAPOR PRESSURE OF SO_2
IN SODIUM SULFITE - BISULFITE SOLUTION
[S (IV)] = 6.012, 323 K

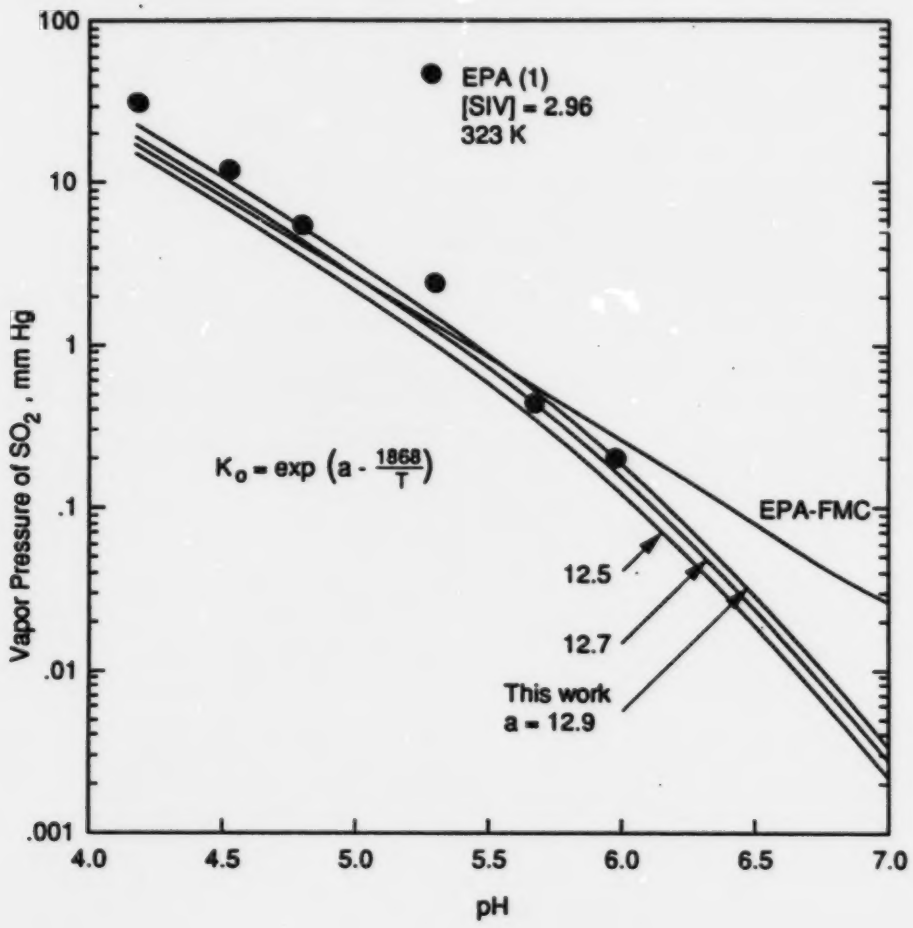

FIGURE 6

VAPOR PRESSURE OF SO_2 IN SODIUM SULFITE-BISULFITE SOLUTION [S(IV)] = 2.96 323 K

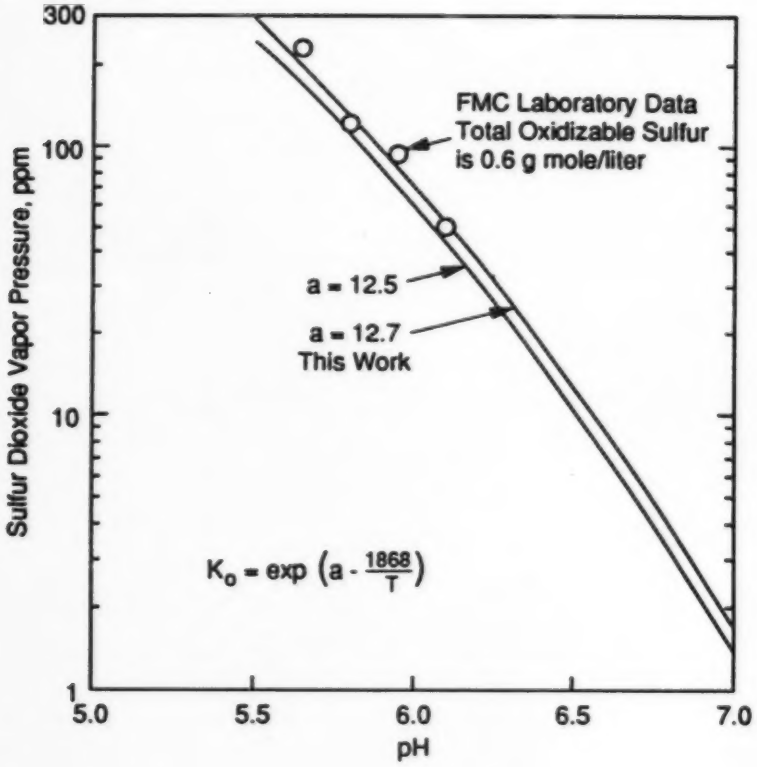

FIGURE 7

**CONCENTRATED ACTIVE DUAL ALKALI SYSTEMS:
SULFUR DIOXIDE VAPOR PRESSURE VS. pH @ 54°C**

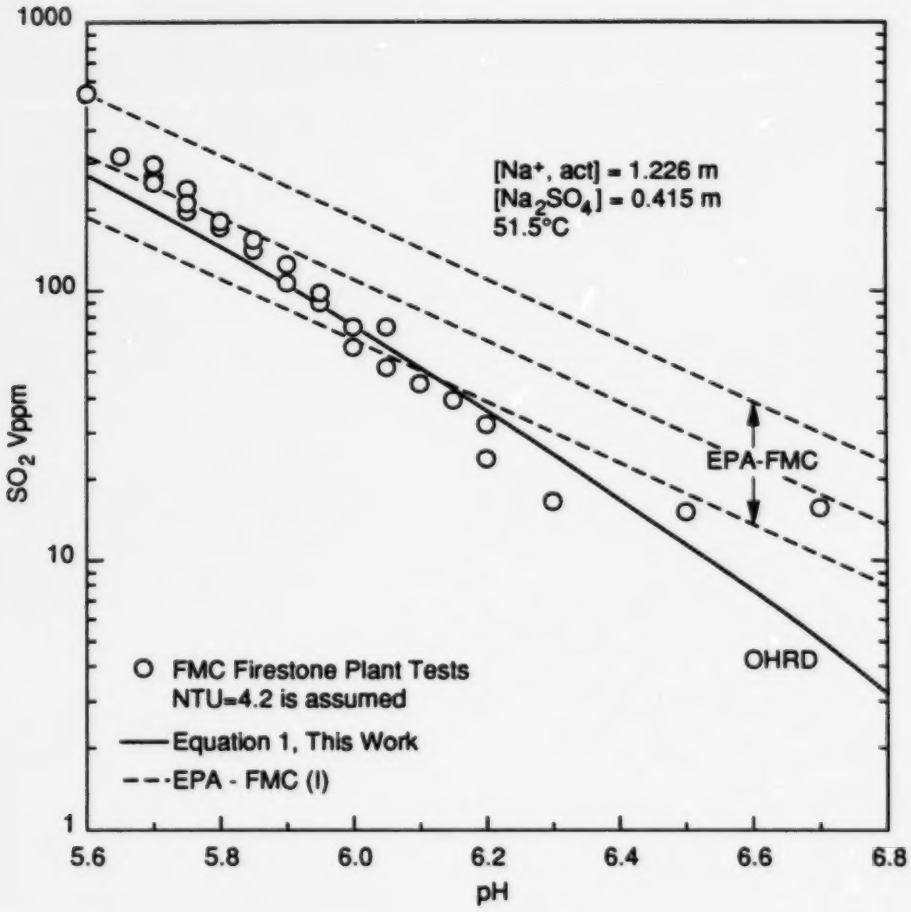

FIGURE 8

PARTIAL PRESSURE OF SO_2 OVER SODIUM BISULFITE - SULFITE AQUEOUS SOLUTION

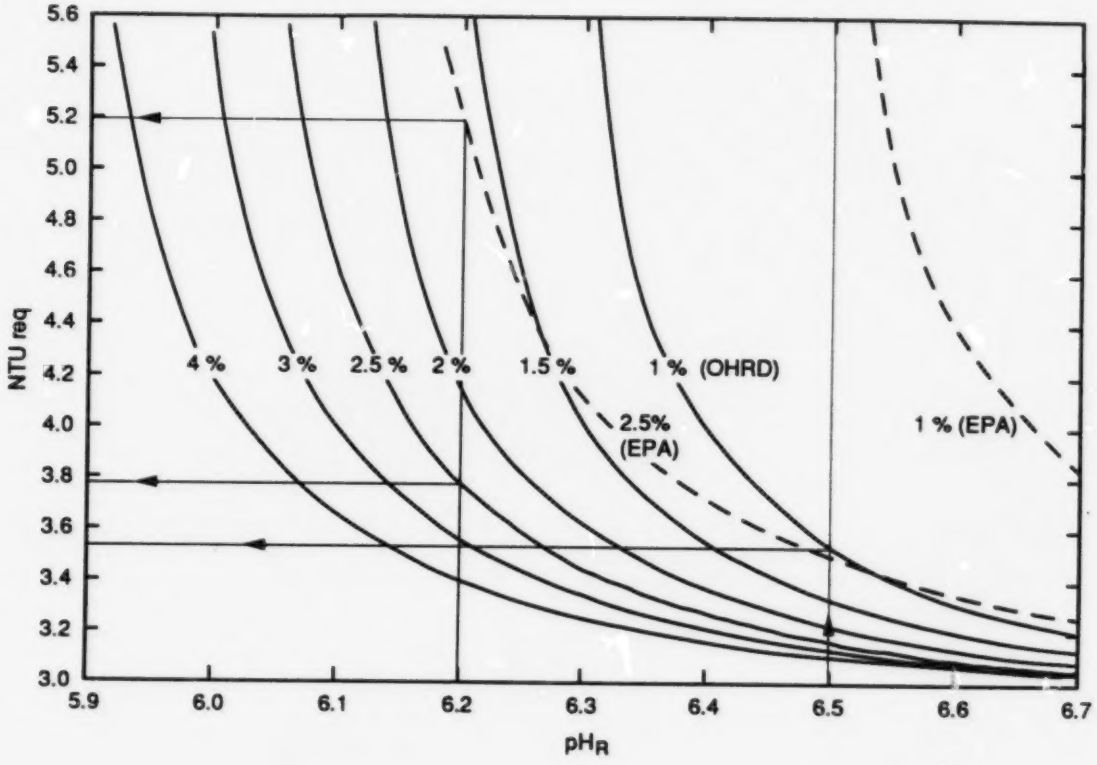

FIGURE 9

EFFECT OF pH AND INLET SO_2 CONCENTRATIONS ON NTU REQUIREMENTS

APPENDIX A

USEFUL RELATIONSHIPS

1. Express the solubility of SO_2 in terms of pH and TOS.

$$m = \frac{TOS}{\left[1 + \frac{K_1 \gamma_{H_2SO_3}}{10^{-pH}\gamma_{HSO_3^-}} + \frac{K_1 K_2 \gamma_{H_2SO_3}}{(10^{-pH})^2 \gamma_{SO_3^-}}\right]}$$

2. Express the solubility of SO_2 in terms of pH and active $[Na^+]$

$$m = \frac{[m_3 + m_1 - 2m_6 - m_8]}{\frac{K_1 \gamma_{H_2SO_3}}{10^{-pH}\gamma_{HSO_3^-}} + \frac{2K_1 K_2 \gamma_{H_2SO_3}}{(10^{-pH})^2 \gamma_{SO_3^-}}}$$

3. Express other compositions in terms of SO_2 solubility

$$m_4 = \left(\frac{K_1 \gamma_{H_2SO_3}}{10^{-pH}\gamma_{HSO_3^-}}\right) m$$

$$m_2 = \left(\frac{K_1 K_2 \gamma_{H_2SO_3}}{(10^{-pH})^2 \gamma_{SO_3^-}}\right) m$$

4. Electron neutrality

$$m_3 + m_1 = 2m_2 + m_4 + 2m_6 + m_8$$

5. Express other compositions in terms of R

$$R = [HSO_3^-]/[SO_3^=]$$

$$[TOS] = [HSO_3^-] + [SO_3^=]$$

$$[SO_3^=] = [TOS]/(1+R)$$

$$[HSO_3^-] = [TOS]\ R/(1+R)$$

$$Act[Na^+] = [TOS](1+1/(1+R))$$

6. Implicit expression of pH in terms of R

$$(10^{-pH})^2 + \left(\frac{1}{2+R}\right)\left(\frac{K_1}{\gamma_{HSO_3^-}}\right)(10^{-pH}) - \left(\frac{R}{R+2}\right)\frac{K_1K_2}{\gamma_{SO_3^-}} = 0$$

or

$$2 \times 10^{-pH} = -\left(\frac{1}{2+R}\right)\left(\frac{K_1}{\gamma_{HSO_3^-}}\right) + \left(\left(\frac{1}{2+R}\ \frac{K_1}{\gamma_{SO_3^-}}\right)^2 + 4\left(\frac{R}{2+R}\right)\frac{K_1K_2}{\gamma_{SO_3^-}}\right)^{1/2}$$

7. Calculate K_2 from pH measurements

$$K_2 = \frac{10^{-pH}\gamma_{SO_3^-}}{R}\left(\frac{10^{-pH}(2+R)}{K_1} + \frac{1}{\gamma_{HSO_3^-}}\right)$$

$$pK_2 = -\log_{10} K_2 = a + \frac{b}{T}$$

APPENDIX B

SCRUBBER PERFORMANCE TESTS

Time	Solution pH	SO_2 Outlet ppm	Venturi Flow (line pressure drop)
1455 Shut off flow to/from regeneration and from soda ash tank to allow pH to drop			
1505	6.7	36	116 gpm (24")
1508	6.5	35.5	
1514	6.3	37	
1516	6.2	45	
1518	6.2	54	
1520	6.15	62	
1522	6.1	69	
1525	6.05	76	
1527	6.0	88	
1529	6.0	101	
1531	5.95	120	
1535	5.9	138	
1538	5.9	160	
1541	5.85	176	
1543	5.85	192	
1546	5.8	210	
1548	5.75	250	
1552	5.7	300	
1554	5.7	350	
1558	5.65	370	
1600	5.6	625	
purged sample line + respanned instrument began flow to/from regeneration to bring pH up			
1605	5.6	610	
1607	5.7	315	
1610	5.75	285	
1612	5.75	255	
1614	5.75	240	
1616	5.8	220	
1619	5.85	185	
1621	5.95	128	
1623	6.05	100	
1625	6.05	75	

APPENDIX C

VAPOR PRESSURE DATA FROM TWR-EPA FIELD TESTS AT FIRESTONE TIRE AND RUBBER PLANT

pH	SO_2, vppm outlet, dry	SO_2, vppm outlet, wet	SO_2, vppm in equilibrium	Calculated SO_2, vppm in equilibrium	EPA Calculated vppm		
6.7	36	31.9	15.6	4.9	29.9	17.7	10.5
6.5	35.5	31.4	15.2	11.2	50.4	29.8	17.7
6.3	37	32.7	15.5	24.8	85.7	50.8	30.1
6.2	45	39.8	23.7	36.4	112	66.4	39.3
6.2	54	47.8	31.8	36.4	112	66.4	39.3
6.15	62	54.9	39.0	43.8	128	76.0	45.0
6.1	69	61.1	45.3	52.7	147	87.0	51.5
6.05	76	67.3	51.6	63.0	168	99.5	59.0
b	88	77.9	62.3	75.2	192	114	67.5
6	101	89.4	74.0	75.2	192	114	67.5
5.95	120	106	91.1	89.4	220	130	77.2
5.9	138	122	107	106	252	149	88.3
5.9	160	142	127	106	252	149	88.3
5.85	176	156	141	125	287	170	101
5.85	192	170	156	125	287	170	101
5.88	210	186	172	147	328	195	115
5.75	250	221	208	173	375	222	132
5.70	300	265	253	202	427	253	150
5.7	350	310	298	202	427	253	150
5.65	370	327	316	236	487	289	171
5.6	625	553	545	275	555	329	195
5.6	610	540	531	275	555	329	195
5.7	315	279	266	202	427	253	150
5.75	285	252	239	173	375	222	132
5.75	255	225	212	173	375	222	132
5.75	240	212	199	173	375	222	132
5.8	220	195	181	147	328	195	115
5.85	185	164	149	125	287	170	101
5.95	128	113	99.3	89.4	220	130	77.2
6.05	100	88.5	73.1	63.0	168	99.5	59.0
6.05	75	66.4	50.7	63.0	168	99.5	59.0